

# Composite Electrolytes for Lithium Batteries: Ionic Liquids in APTES Crosslinked Polymers

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## Abstract

Solvent free polymer electrolytes were made consisting of Li<sup>+</sup> and pyrrolidinium salts of trifluoromethanesulfonimide added to a series of hyperbranched poly(ethylene oxide)s (PEO). The polymers were connected by triazine linkages and crosslinked by a sol-gel process to provide mechanical strength. The connecting PEO groups were varied to help understand the effects of polymer structure on electrolyte conductivity in the presence of ionic liquids. Polymers were also made that contain poly(dimethylsiloxane) groups, which provide increased flexibility without interacting with lithium ions. When large amounts of ionic liquid are added, there is little dependence of conductivity on the polymer structure. However, when smaller amounts of ionic liquid are added, the inherent conductivity of the polymer becomes a factor. These electrolytes are more conductive than those made with high molecular weight PEO imbibed with ionic liquids at ambient temperatures, due to the amorphous nature of the polymer.

## Introduction

Rechargeable lithium-polymer batteries offer several advantages over their liquid and gel electrolyte counterparts.<sup>1</sup> Replacing flammable solvent with a polymer electrolyte potentially improves battery safety, increases design flexibility and improves mechanical strength. Also, polymers such as poly(ethylene oxide) (PEO) doped with a lithium salt show excellent stability toward lithium metal compared to the most popular liquid electrolytes. Hence, the energy density of the battery would be enhanced by replacing the typical graphite intercalation anode with a lithium metal anode.<sup>2,3</sup>

Despite the advantages of using solid polymer electrolytes in lithium batteries, they are slow to reach the commercial market because of low electrolyte conductivities at ambient temperatures. Lithium ion conductivities above 10<sup>-3</sup> S/cm are generally considered a requirement for battery operation.<sup>4</sup> However, polymer electrolytes for

lithium batteries appear to reach an upper limit below  $10^{-4}$  S/cm at room temperature. In addition, most processes that improve the conductivity of the polymer electrolyte either tend to decrease dimensional stability or require a very cumbersome synthetic approach.<sup>5-7</sup>

Low conductivity in polymer electrolytes have recently been addressed by Shin and coworkers by the addition of room temperature ionic liquids (RTILs) to PEO.<sup>8-12</sup> Ionic liquids typically consist of an asymmetric organic cation and a bulky anion with a highly delocalized charge to minimize packing. RTILs are both nonvolatile and nonflammable, thereby maintaining the safety advantage of the polymer electrolyte while adding a liquid component. The RTILs used in this study consisted of N-butyl-N-methylpyrrolidinium trifluoromethanesulfonimide ( $P_{14}$ , Scheme 1), and N-propyl-N-methylpyrrolidinium trifluoromethanesulfonimide ( $P_{13}$ ).<sup>13-16</sup> These RTILs have been shown to be stable toward lithium metal when mixed with LiTFSi.<sup>16</sup> When 30 wt% of  $P_{13}$  is added to PEO doped with LiTFSi, more than an order of magnitude increase in conductivity is reported. Moreover, they were able make dimensionally stable films that contained as much as 150%  $P_{13}$ .<sup>8</sup> They also report that the contribution of lithium ions toward conductivity is similar to the ratio of ions within the polymer film. This is surprising since  $Li^+$  is the only ion present that should be solvated by the polymer network. Thus, there is still not a full understanding of the interaction between the polymer, ionic liquid, and lithium salt within the polymer electrolyte.

Our laboratory has recently reported the synthesis of novel hyperbranched polymer electrolytes that contain PEO-based oligomers connected via a triazine linkage.<sup>17</sup> The polymers are crosslinked by addition of 3-aminopropyltriethoxysilane (APTES) to improve dimensional stability. When doped with LiTFSi, these polymers are amorphous at room temperature. Unlike with PEO, it is easy to change the composition and properties of the polymer backbone, crosslink density and sidechains by simply changing the amount and type of monomer units. These factors make the system an ideal candidate to understand the effects of polymer structure on the polymer-ionic liquid-lithium salt system. In this paper, we report the synthesis of several forms of the triazine linked polymers containing several RTILs. Conductivity was then measured as a function of IL cation, IL concentration, polymer branching, and degree of crosslinking. For further comparison, polymers were synthesized in which  $Li^+$ -coordinating PEO was partially replaced by poly(dimethylsiloxane) (PDMS), with which  $Li^+$  should have little interaction. Films from commercial PEO and poly(vinylidene fluoride-co-hexafluoropropylene) PVDF(HFP) containing the same RTIL were also prepared for comparison..

## Experimental

**Materials.** Cyanuric chloride, and (3-aminopropyl)triethoxysilane (APTES) were purchased from Aldrich Chemical Company and used as received. Diisopropylethylamine was purchased from Aldrich in Biotech grade and used as received. Lithium bis(trifluoromethane)sulfonimide (LiTFSi) was purchased from 3M, dried at  $140^{\circ}C$  under vacuum for 10 hours, and stored in a dry box. Monoamine and diamine-capped polyalkylene oxide oligomers (Jeffamine XTJ-500, XTJ-502, XTJ-234, and XTJ-506) were kindly supplied by Huntsman Corporation. The diamine endcapped poly(dimethylsiloxane) oligomer of MW = 3066 was purchased from Aldrich. The

diamine endcapped poly(dimethylsiloxane) oligomer of MW = 842 (DMS-A11) was purchased from Gelest Inc.. The molecular weights of the PDMS oligomers were determined through  $^1\text{H}$  NMR endgroup analysis. All glassware was oven-dried for at least 24 hours prior to use. N-butyl-N-methylpyrrolidinium trifluoromethanesulfonimide ( $\text{P}_{14}$ ), N-propyl-N-methylpyrrolidinium trifluoromethanesulfonimide ( $\text{P}_{13}$ ), and N-(2-methoxyethyl)-N-methylpyrrolidinium trifluoromethanesulfonimide ( $\text{P}_{1(2\text{O}1)}$ ) (Scheme 1) were synthesized and purified according to a literature procedure to give clear liquids.<sup>8-11</sup> PEO ( $M_w = 5 \times 10^6$ ) and was purchased from Aldrich and used as received. PVDF(HFP) was kindly provided by Elf Atochem as Kynar Flex 2801 and used as received.

APTES crosslinked hyperbranched polymers were synthesized as reported previously.<sup>17</sup> In polymers that contained PDMS segments, diamine-endcapped PDMS oligomers were dissolved in THF at the same time as the diamine-endcapped PEO oligomers before the addition of cyanuric chloride. Ionic liquids were added to solutions of the non-crosslinked polymer and LiTFSi in THF, and then cast into films in Teflon® boats. The resulting films were cured at 160°C under vacuum. The ionic liquids could also be added to the cured films, but the films had to be swollen with THF to ensure a uniform composition. Therefore the first method of RTIL imbibing was preferred. To films that contained only PEO oligomers, LiTFSi was added to obtain a ratio of 20:1 ether oxygen:lithium. Subsequent films made from PDMS oligomers, as well as PVDF(HFP), contained the same amount of lithium salt as polymer A from Table 1. The polymer film from PEO (20:1 O:Li) and 150%  $\text{P}_{13}$  was made by hot-pressing the sample according to a literature procedure.<sup>8</sup> The film made from PVDF(HFP) was cast from NMP, then dried under vacuum at 70°C for 24 hrs and 200°C for 2 hrs.

**Instrumentation.** Polymers were characterized by differential scanning calorimetry (DSC) from -90 to 300°C using a Q1000 calorimeter manufactured by TA Instruments. Thermal gravimetric analysis (TGA) was obtained using a TA instruments high resolution TGA2950 analyzer. ATR-FTIR spectra of polymer films were taken with a Nicolet Nexus 470 FTIR spectrometer equipped with a Smart Omni sample ATR accessory.

Ionic conductivity was measured between stainless steel electrodes by electrochemical impedance techniques, using a Solartron/Schlumberger model 1250 FRA and model 1286 Electrochemical Interface.<sup>18,19</sup> Conductivity was measured over the range of 0 to 80°C. Coin cells were made from a film of electrolyte sandwiched between 5/8" diameter lithium discs under internal pressure. Cells were heated to 40°C and cycled at  $\pm 50 \text{ uA/cm}^2$  and  $\pm 100 \text{ uA/cm}^2$  current density. Cycles used a 3-hour current application followed by a 1-hour rest. A polarization limit of 2-Volt was included to minimize deterioration of the SPE

## Results and Discussion

In a previous study,<sup>17</sup> we synthesized a series of polymers by the reaction of cyanuric chloride with diamine endcapped poly(alkylene oxide) oligomers of molecular weights 600 and 2000 (shown in Scheme 2).<sup>20</sup> The third reactive site on cyanuric chloride was then functionalized with either a poly(alkylene oxide) or a crosslinking group. These polymers were doped with LiTFSi to form polymer electrolytes, and optimized for ionic conductivity and mechanical integrity. The most conductive polymer that forms a

dimensionally stable film from that study is the structure identified in Scheme 3 as polymer **B**. Polymer **C**, also shown in Scheme 3 was the least conductive, but strongest mechanically. The ionic conductivity of polymer **A** is between polymers **B** and **C**, but **A** has the simplest molecular structure, being composed of only one diamine oligomer. Polymer electrolytes were made from these three polymers, LiTFSi, and three different pyrrolidinium cation based ionic liquids. Figure 1 shows that when polymer **A** is imbibed with 1.5 times its weight in RTIL, the film containing P<sub>13</sub> is the most conductive. Solutions of 0.5 mol/kg LiTFSi in P<sub>13</sub> have also been reported as slightly more conductive than solutions of LiTFSi in P<sub>14</sub>,<sup>16</sup> possibly due to the lower viscosity of P<sub>13</sub>. The conductivity of polymer **B** imbibed with P<sub>13</sub> is also higher than P<sub>14</sub> and P<sub>1(201)</sub> at 25°C (Table 1), but in this case the difference is smaller.

Figure 2 shows that the addition of 30 wt% P<sub>13</sub> to polymer **A** increases the conductivity by almost an order of magnitude at lower temperatures. The conductivity continues to increase as more RTIL is added. These results are similar to that obtained with PEO<sup>8</sup> at higher concentrations of RTIL. At lower RTIL loadings ( $\leq 50\%$ ), the low temperature conductivities for polymer **A** are slightly higher than that reported for PEO presumably because polymer **A** completely amorphous before the addition of any RTIL.<sup>17</sup>

Figure 3 shows the effects of adding RTIL to polymers of different composition. The addition of P<sub>13</sub> tends to provide a sharper increase to the less conductive electrolytes. The addition of 50% P<sub>13</sub> to polymers **A**, **B**, and **C** increase the conductivity by a factor of 10, 5, and 50, respectively. When 150% P<sub>13</sub> is added to these three polymers, the conductivity profile as a function of temperature is almost indistinguishable. This data gives reason to believe that within this set of polymers, conductivity is dictated by both the polymer composition and amount of ionic liquid at lower P<sub>13</sub> concentrations. However, at high RTIL concentrations, conductivity is dictated by the RTIL only. For example, polymer **B** is almost 40 times as conductive as polymer **C** at ambient temperatures. At 150% P<sub>13</sub>, the difference is less than a factor of 1.5. The plasticizing effect of P<sub>13</sub> on these polymers should also be noted, as shown by their  $T_g$  values in Table 1. The  $T_g$  in the absence of RTIL ranges from -37°C for polymer **C** to -52°C for polymer **B**. No decrease in the  $T_g$  is observed at 30% P<sub>13</sub>, followed by small decreases at 50% P<sub>13</sub>. When 150% P<sub>13</sub> is added, the  $T_g$  for all three polymers become very similar (-64°C to -68°C).

Although all three polymers exhibit similar conductivities at high loadings of P<sub>13</sub>, it is possible that Li<sup>+</sup> mobility is limited by coordination to PEO. To help provide further insight toward this issue, the PEO oligomers in polymer **B** were partially replaced with poly(dimethylsiloxane) (PDMS) oligomers. PDMS oligomers were chosen because of their oxidative stability, high free volume, and flexibility. PDMS has a  $T_g \sim -120^\circ\text{C}$ . In addition, PDMS will not bind to lithium ions. Initially, polymers were made in the same fashion as polymer **B**, with PEO-diamines completely replaced by PDMS-diamines. However, both the polymer solutions and resulting films were immiscible with the ionic liquids. When 50 wt% XTJ-502 and 50 wt% PDMS was used, the solutions became miscible and the films uniform. When a longer PDMS (40 repeat units) oligomer was used, these polymers had a difficult time holding on to large quantities of RTIL. Hence, the polymers with shorter PDMS (10 repeat units) oligomers were used.

Comparison of the conductivity vs. temperature of polymer **E** (from Scheme 3) with polymer **A** is shown in Figure 4. When no RTIL is added, **B** is much more conductive

than **E**. This is probably due to better ion dissociation of the lithium salt. When only 50%  $P_{13}$  is added, these conductivities become almost identical. Furthermore, there is a more substantial decrease in the  $T_g$  of polymer **E** at low amounts of RTIL loading (Table 2), suggesting a stronger plasticizing effect than in polymer **A**. As with **A**, **B**, and **C**, at 150%  $P_{13}$  the conductivities of these two polymers are nearly identical. Polymer **E**, imbided with 150%  $P_{13}$  does reach the highest room temperature conductivity of any of the electrolytes that were studied ( $8.8 \times 10^{-4}$  S/cm at 25°C).

A final conductivity experiment was run in which polymer **A** imbided with 150%  $P_{13}$  was compared to commercially available PEO and PVDF(HFP) imbided with 150%  $P_{13}$ .<sup>21</sup> Polymer **A** is more conductive than both commercial polymers at lower temperatures. The lower conductivity in PEO is most likely due to the presence of less conductive crystalline regions<sup>22,23</sup> within the film, while the PVDF(HFP) film has a less flexible matrix with a higher melt transition. The PVDF(HFP) polymer used has been reported as having a 30% crystalline fraction with a melting point of 142°C.<sup>24</sup> The conductivities of polymer **A** and PEO become similar above ~40°C. This jump in conductivity in PEO matches up well with a melting transition observed previously.<sup>8</sup> This is a very interesting result when polymers **B** and **C** are considered as well. It appears that at 150%  $P_{13}$ , the composition of the PEO-containing polymer makes little difference on conductivity at lower temperatures as long as the crystalline PEO fraction is suppressed.

It has been reported previously that, although freestanding PEO films can be made with large amounts of RTIL, acceptable long term stability toward stripping and plating is only observed with  $\leq 90\%$   $P_{13}$  in  $P(EO)_{20}$ -LiTFSi.<sup>9</sup> The decreased stability above this concentration has been attributed to the presence of “excess” ionic liquid that is not interacting with either PEO or LiTFSi. This free RTIL is not stable in contact with lithium metal. For comparison, stripping and plating was measured within a Li/Polymer **A** +  $xP_{13}$ /Li coin cell, as shown in Figure 6. Samples of polymer **A** contained 50, 100, and 150%  $P_{13}$ , are denoted as cells **X**, **Y**, and **Z**, respectively. Cells were cycled at 40°C at  $\pm 50 \mu\text{A}/\text{cm}^2$  current density for 2 cycles, followed by  $\pm 100 \mu\text{A}/\text{cm}^2$ . Cell **X** shows the best stability. This cell shows an initial jump in polarization, which becomes more stable over the first 4 cycles. The sample then has a stable impedance until a jump in polarization after 170 hours of testing. Resumption of 50  $\mu\text{A}$  cycles shows stable polarization with a small impedance increase. Cell **Y** also shows an initial increase in polarization. However, the cycling stability does not improve after this increase. After 100 hours of testing, the cell rapidly polarizes to the 2-Volt limit. The cell with 150%  $P_{13}$  shows the worst long term stability. After 70 hours, the cell rapidly polarizes to the 2-Volt limit. Resumption of cycles at 50  $\mu\text{A}$  shows permanent increase in polarization. It appears that only the sample with 50%  $P_{13}$  is able to form a stable SEI. It was noted that the interfacial impedance of cell **X** increases after one day of testing, followed by a decrease after 10 days, although not down the original level. In cells **Y** and **Z**, the interfacial impedance increases after 1 day, and further increases after 10 days.

Cycling was also performed on polymer **E**. In this case, cycling stability was poor. The instability appears to originate from the polymer, since stability increased when increasing amounts of RTIL were added.

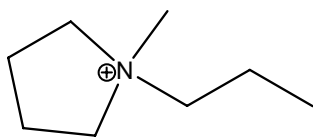
## Conclusions

Five different polymers were made by the reaction of diamine terminated oligomers with cyanuric chloride, followed by further reaction with either a branching or crosslinking group. Three polymers were made solely from PEO based oligomers, which had varying degrees of conductivity when no ionic liquid were added. The other two polymers also contained PDMS oligomers. The polymers were combined with LiTFSi and ionic liquids to form polymer electrolytes. In films that contain high amounts of RTIL (150%), electrolyte conductivity does not depend on the polymer structure. However, the polymers only appear to be stable toward Li cycling at lower RTIL levels (between 50 and 100%). In this case, the conductivity also depends upon the polymer structure. At lower RTIL levels, these polymers are completely amorphous at ambient temperatures, giving them an inherent advantage over PEO. These polymers may be better for low temperature use, especially below the melting point of the crystalline PEO fraction. Polymers in which PEO oligomers were partially replaced with more flexible PDMS oligomers did not show a dramatic increase in conductivity at 150% P<sub>13</sub>. Furthermore, these polymers did not hold RTIL as well as polymers with only PEO oligomers.

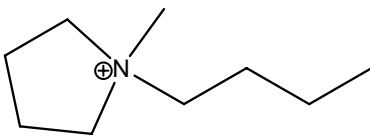
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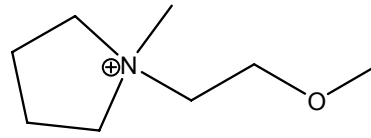
### Cation



P<sub>13</sub>

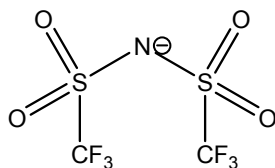


P<sub>14</sub>



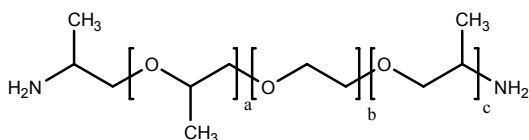
P<sub>1(2O1)</sub>

### Anion



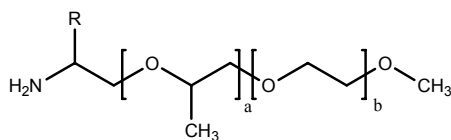
TFSI

**Scheme 1.** Room temperature pyrrolidinium-based ionic liquids.



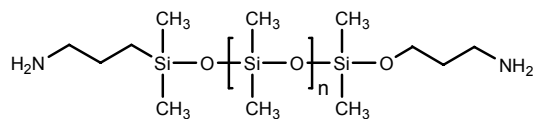
Jeffamine XTJ-502  
b = 39.5  
a + c = 5  
MW = 2000

Jeffamine XTJ-500  
b = 9.0  
a + c = 3.6  
MW = 600



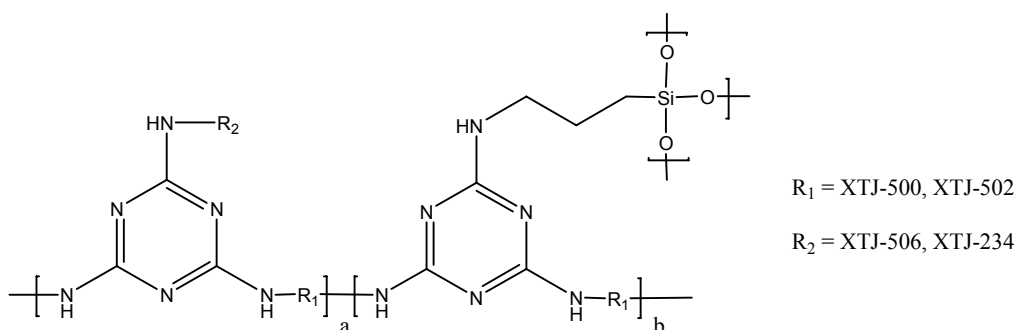
Jeffamine XTJ-506  
EO = 19  
PO = 3  
MW = 1000

Jeffamine XTJ-234  
EO = 49  
PO = 8  
MW = 2620



DMS-3000, n ~ 40  
DMS-A11, n ~ 10

**Scheme 2.** Amine and diamine endcapped oligomers.



Polymer A:  $R_1 = \text{XTJ-502}$ ,  $b = 1$   
 Polymer B:  $R_1 = \text{XTJ-502}$ ,  $R_2 = \text{XTJ-234}$ ,  $a = b = 0.5$   
 Polymer C:  $R_1 = \text{XTJ-500}$ ,  $R_2 = \text{XTJ-506}$ ,  $a = 0.25$ ,  $b = 0.75$   
 Polymer D:  $R_1 = 1:1 \text{ DMS-3000:XTJ-502 by weight}$ ,  $b = 1$   
 Polymer E:  $R_1 = 1:1 \text{ DMS-A11:XTJ-502 by weight}$ ,  $b = 1$

**Scheme 3.** Polymer structure.

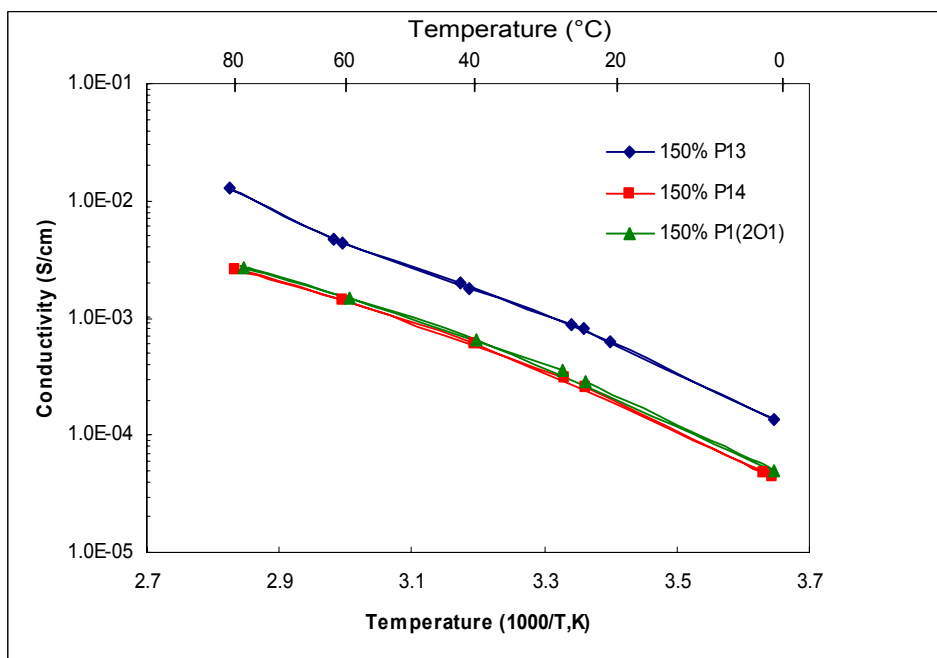
Polymer	Ionic Liquid	Wt% RTIL Added	T <sub>g</sub> (°C)	σ (S/cm, 25°C)
A	none	0	-45.9	1.0E-5
A	P <sub>13</sub>	30	-46.1	7.9E-5
A	P <sub>13</sub>	50	-49.7	1.0E-4
A	P <sub>13</sub>	100	-61.3	4.4E-4
A	P <sub>13</sub>	150	-64.4	7.6E-4
A	P <sub>14</sub>	150	-62.9	5.3E-4
A	P <sub>14O</sub>	150	-66.5	5.9E-4
B	none	0	-52.2	3.7E-5
B	P <sub>13</sub>	30	-48.9	1.2E-4
B	P <sub>13</sub>	50	-53.3	1.9E-4
B	P <sub>13</sub>	150	-64.3	7.2E-4
B	P <sub>14</sub>	30	-51.5	9.0E-5
B	P <sub>14</sub>	50	-52.5	1.6E-4
B	P <sub>14</sub>	150	-64.6	6.7E-4
B	P <sub>14O</sub>	30	-51.1	9.5E-5
B	P <sub>14O</sub>	50	-52.0	1.7E-4
B	P <sub>14O</sub>	150	-63.5	7.1E-4
C	none	0	-37.5	1.3E-6, 9.6E-7
C	P <sub>13</sub>	30	-34.2	1.5E-5
C	P <sub>13</sub>	50	-43.7	5.2E-5
C	P <sub>13</sub>	150	-68.1	5.4E-4

**Table 1.** Thermal and conductivity data for films of polymers **A-C** imbibed with ionic liquids.

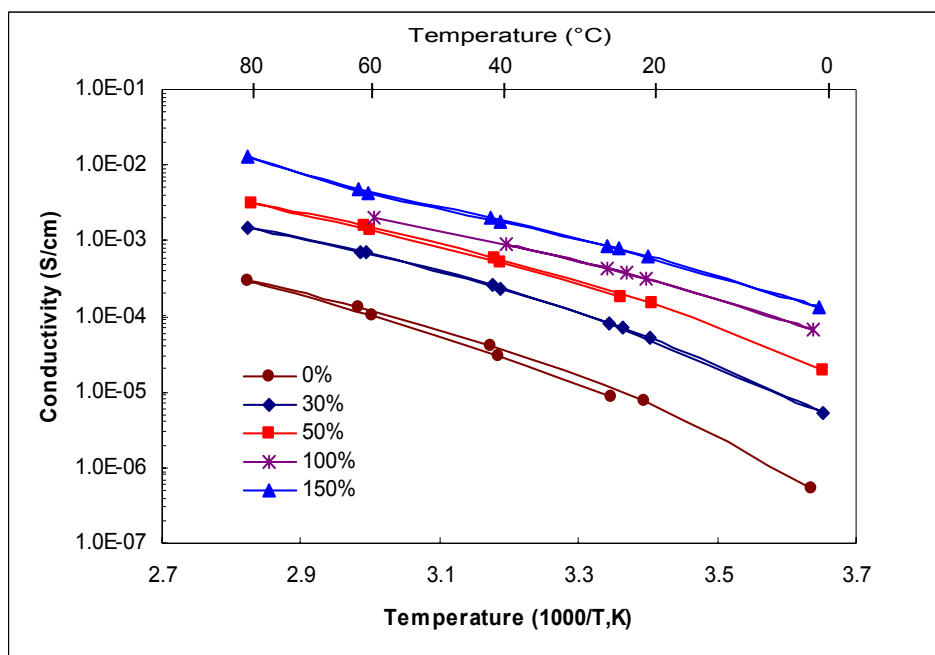


Polymer	Ionic Liquid	PDMS MW	Wt% RTIL Added	T <sub>g</sub> (°C)	$\sigma$ (S/cm, 25°C)
D	P <sub>13</sub>	3066	0	-40.0	1.2E-6
D	P <sub>13</sub>	3066	50	-57.6	a
D	P <sub>13</sub>	3066	100	-69.3	4.4E-4
D	P <sub>13</sub>	3066	150	Not observed	1.0E-4 <sup>b</sup>
D	No additives	3066	0	Not observed	-
E	P <sub>13</sub>	842	0	-47.2	2.8E-6
E	P <sub>13</sub>	842	50	-59.9	1.5E-4
E	P <sub>13</sub>	842	100	-62.2	5.2E-4
E	P <sub>13</sub>	842	150	-69.7	8.8E-4
E	No additives	842	0	-63.3	-

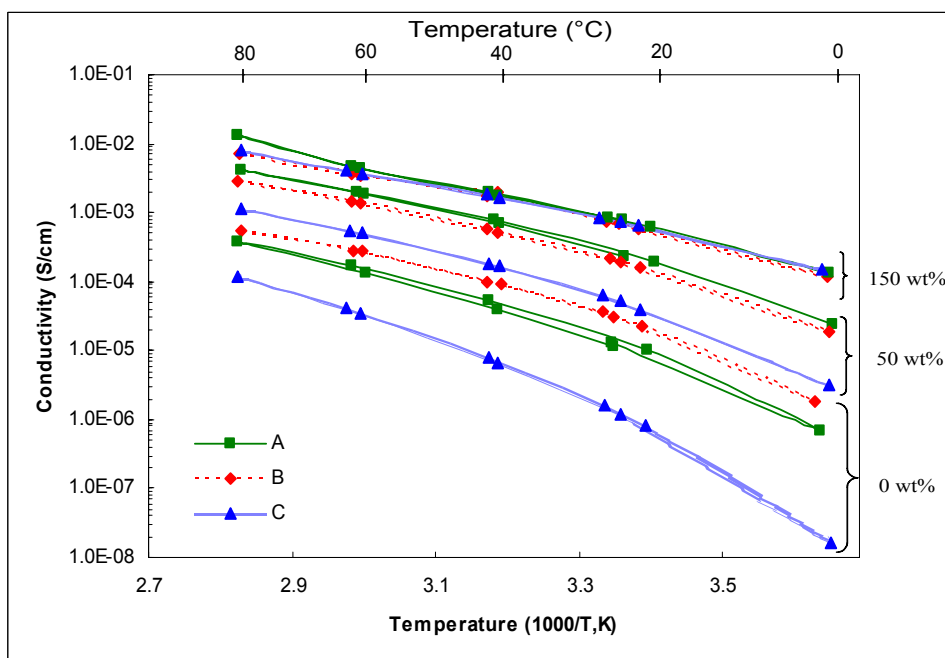
**Table 2.** Thermal and conductivity data for polymer films **D** and **E** imbibed with P<sub>13</sub>. The polymer is made from 50 wt% 2000 PEO diamine and 50 wt% PDMS diamine in the main chain. a) Film was cracked and conductivity could not be measured. b) An oily substance extruded from the sample during testing.



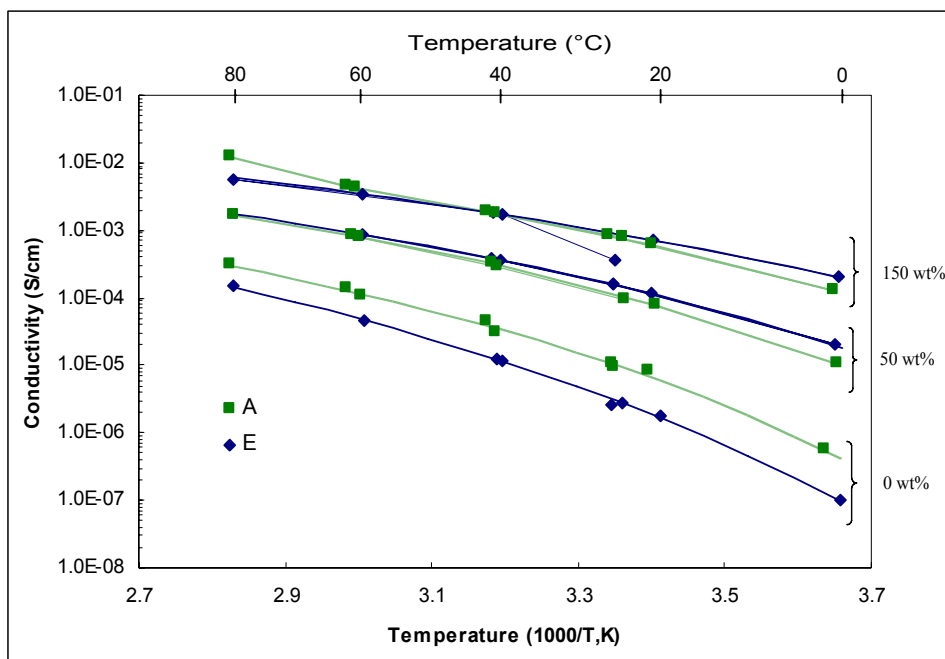
**Figure 1.** Conductivity as a function of temperature for films of polymer **A** that contain 150 wt% of various ionic liquids.



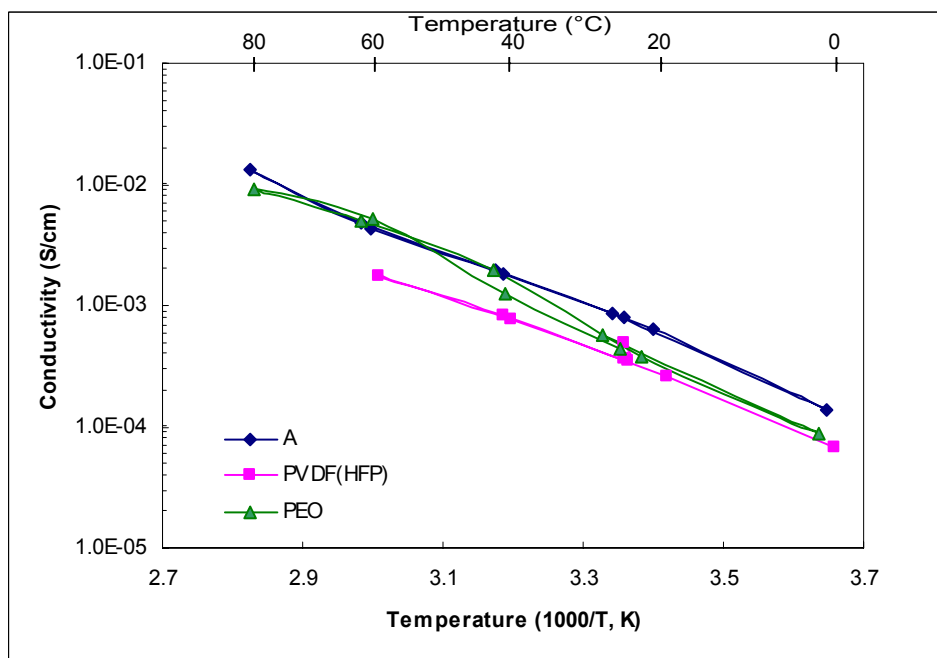
**Figure 2.** Conductivity as a function of temperature for films of polymer **A** that contain various amounts of  $P_{13}$ .



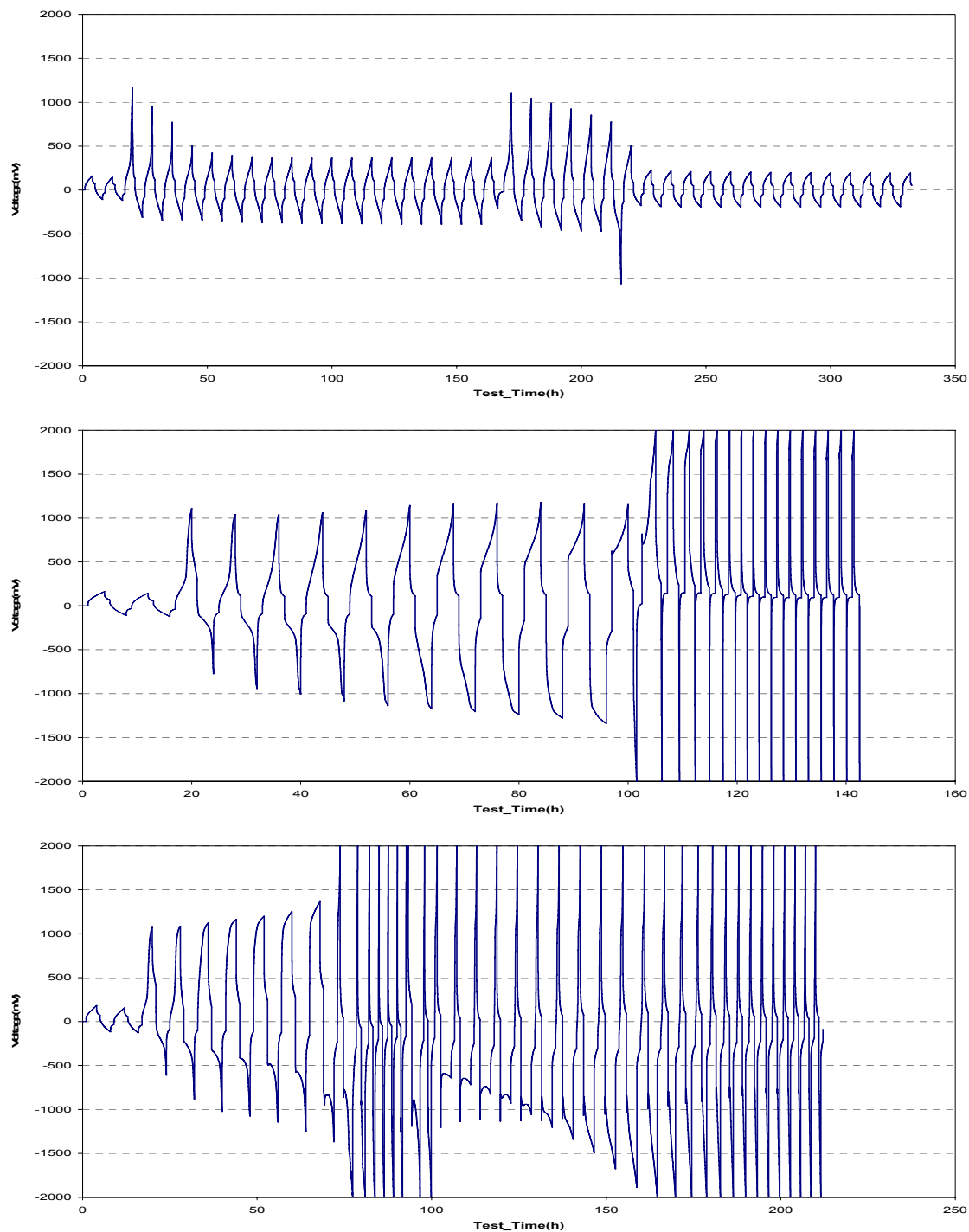
**Figure 3.** Conductivity as a function of temperature for polymer films **A**, **B**, and **C** that contain 0 wt% (bottom three lines), 50 wt% (middle three lines), and 150 wt% (top three lines)  $P_{13}$ .



**Figure 4.** Conductivity as a function of temperature for polymer films **A** and **E** that contain 0 wt% (bottom two lines), 50 wt% (middle two lines), and 150 wt% (top two lines)  $P_{13}$ .



**Figure 5.** Conductivity as a function of temperature for polymer **A** compared to PEO and PVDF(HFP). 150%  $P_{13}$  was added to each film.



**Figure 6.** Cycling behavior of a Li/Polymer A + x wt% P<sub>13</sub>/Li cell during stripping/plating at 40°C. From top to bottom, the polymer contains 50, 100, and 150% P<sub>13</sub>.